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## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : MITSUBISHI CHEM CORP  
MITSUBISHI GAS CHEM CO INC

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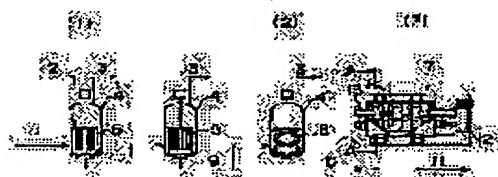
(72)Inventor : KUMAZAWA KATSUHISA  
KAWAI MICHIO  
HAYASHI KATSUSHIGE  
TAKEDA YUJI

### (54) PRODUCTION OF AROMATIC POLYCARBONATE RESIN

#### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a high-molecular-weight aromatic polycarbonate resin having excellent hue.

**SOLUTION:** This resin is produced by transesterifying an aromatic diol compound with a carbonic diester in the preliminary polycondensation step 1 using an upright reactor 4 with an agitator to produce a first prepolymer, converting the first prepolymer into a second prepolymer in the prepolycondensation step 2 using an upright reactor 4 with an agitator consisting of a double-helical ribbon blade, leading the second prepolymer to a horizontal reactor 7 in which grid type agitating blades 8 each of which is formed by juxtaposing two rotary trunnion and connecting a plurality of rodlike rectangular frames to each trunnion in the proximity of the inside of the mating blade so as to mesh with each other, and subjecting the second prepolymer to a polycondensation reaction.



**[Claim(s)]**

**[Claim 1]** In the approach of carrying out the ester exchange reaction of an aromatic series diol compound and the carbonic acid diester, and manufacturing aromatic series polycarbonate resin The melting mixture of an aromatic series diol compound and carbonic acid diester is supplied in a vertical-type churning reactor. (1) — reserve polycondensation process: — After performing the polycondensation reaction of mixture and manufacturing the 1st prepolymer of viscosity average molecular weight 3,000–10,000, (2) — last polycondensation process: — the 1st prepolymer obtained at the process of the above (1) It leads to the vertical-type churning reactor possessing a double helical ribbon aerofoil, and a polycondensation reaction is performed within this reactor and viscosity average molecular weight makes with the 2nd prepolymer of 10,000–20,000. Subsequently (3) — back polycondensation process: — the 2nd prepolymer of said process (2) — the end lower part of the container longitudinal direction of a horizontal type — It has the inlet port of a processed liquid, an outlet, and the exhaust port of volatile matter in the other end lower part and the upper part, respectively. Install two rotation \*\*\*\* in the longitudinal direction both ends inside a container side by side, connect two or more cylindrical rectangle frames with each of this rotation \*\*\*\*, and a skeleton pattern impeller is formed. It leads in the horizontal-type reactor which approaches inside the impeller of the other party and rotates so that this impeller may gear mutually. The manufacture approach of the aromatic series polycarbonate resin which performs a polycondensation reaction, is the amount of nearby giant molecules and is characterized by viscosity average molecular weight obtaining the aromatic series polycarbonate resin of 15,000–40,000 from the 2nd prepolymer of the above (2).

**[Claim 2]** The manufacture approach of the aromatic series polycarbonate resin according to claim 1 which is the vertical-type churning reaction vessel in which the vertical-type churning reaction vessel used at a reserve polycondensation process possesses the Max blend aerofoil.

**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the approach of manufacturing in more detail the aromatic series polycarbonate by which thermal resistance has been improved from an aromatic series diol compound and carbonic acid diester at a melt polycondensation reaction, about the manufacturing method of the polycarbonate by the ester exchange reaction.

**[0002]**

**[Description of the Prior Art]** In recent years, the aromatic series polycarbonate is broadly used in many fields, such as a carbonated drink bottle, an electronic substrate (CD substrate), and an imprint belt, as engineering plastics which were excellent in mechanical properties, such as shock resistance, and were moreover excellent in thermal resistance, transparency, etc.

**[0003]** As the manufacture approach of this aromatic series polycarbonate, the so-called phosgene method to which aromatic series diol and phosgenes, such as a bisphenol, are made to react by the interfacial polycondensation method is industrialized. However, troubles, such as corrosion when using this for electronic equipment, are pointed out by mixing into that this phosgene method must use a poisonous phosgene for the body, and the generation polymer of the sodium chloride which carries out a byproduction so much.

**[0004]** Moreover, the method of obtaining an aromatic series polycarbonate by the ester exchange reaction of an aromatic series diol compound and carbonic acid diester is also learned as the so-called scorification or a non phosgene method for many years. The non phosgene method does not have various troubles of the phosgene method like the above, either, and is supposed that it has the advantage that an aromatic series polycarbonate can be manufactured more cheaply. However, there was a trouble that the viscosity of a reaction mixture becomes high with the rise of the molecular weight of an aromatic series polycarbonate since the non phosgene method is the bulk-polymerization reacting method, and it became difficult to remove by-products, such as a phenol, from a reaction mixture efficiently in a polymerization process anaphase.

**[0005]** In order to solve this trouble, after manufacturing the prepolymer of low molecular weight comparatively at a pre-polymerization process generally, the two-step polymerization method which performs macromolecule quantification according to a postpolymerization process is known. As this postpolymerization process, the approach using the horizontal-type polymerization equipment of hyperviscous correspondence and the approach using horizontal-type polymerization equipment although there is a method of performing solid state polymerization etc. can obtain a polymer with sufficient productivity, and are industrially used as an advantageous approach. In this two-step polymerization method, using the equipment which has a special churning form is proposed variously. For example, after a tank reactor performs a polycondensation reaction in the approach of carrying out melt polycondensation of the bis-aryl carbonate to an aromatic series diol compound by the ester interchange method, and manufacturing an aromatic series polycarbonate, at least one or more sets of paddle form self-cleaning twin screw extruders are used, and the manufacturing method which obtains the aromatic series polycarbonate of viscosity average molecular weight 12,000-60,000 is indicated by JP,4-142329,A.

**[0006]** However, since application of the paddle form self-cleaning twin screw extruder to the last production process used as a hyperviscous processing field was the impeller of a high shear mold, its churning generation of heat was large, and it had the trouble of worsening the hue of the aromatic series polycarbonate obtained. Moreover, the polymerization method which carries out the polycondensation of the polycarbonate prepolymer which are mean molecular weights 5,000-10,000 to JP,7-330910,A using the churning equipment which has a revolving shaft in the upper part inside a container, connects the impeller of the shape of two or more rectangle frame to this revolving shaft about the continuation polymerization method of a polycondensation system macromolecule, and scratches a container wall, and is characterized by obtaining the middle polymerization object which are mean molecular weights 10,000-20,000 is indicated. However, in the above-mentioned molecular weight range, the viscosity of processing liquid is hundreds - about 1000poise of numbers, and in order application of this equipment in this

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molecular weight field is not necessarily excellent in the renewal nature of a front face to the gas-liquid interface by churning operation of the polymerization liquid in a tub and to make predetermined molecular weight reach, it has the problem that require the residence time of long duration and the hue of the aromatic series polycarbonate obtain by the heat history of long duration gets worse.

[0007] Furthermore, in the manufacture approach of the aromatic series polycarbonate currently indicated by JP,2-153925,A, since the polymerization is carried out to the level rotation shaft using the horizontal-type polymerization equipment which has the impeller attached perpendicularly, inevitably, a polymer tends to pile up in the part of a level rotation shaft etc. which does not contribute to churning directly, and the coloring of a polymer and generating of unnecessary gel which are acquired arise. Moreover, although the example of manufacture of the polycarbonate using the extruder polymerization equipment which combined the screw and the paddle was indicated by JP,63-23926,A, it was easy to produce stagnation of the polymer in the discontinuous part of a wing too, and there was a problem of coloring or a physical-properties fall.

[0008]

[Problem(s) to be Solved by the Invention] The purpose of this invention solves the trouble of the above conventional techniques, and is to offer the approach of manufacturing to stability the aromatic series polycarbonate of the amount of giant molecules which is excellent in a hue for a short time.

[0009]

[Means for Solving the Problem] In the approach of this invention carrying out the ester exchange reaction of an aromatic series diol compound and the carbonic acid diester, and manufacturing aromatic series polycarbonate resin The melting mixture of an aromatic series diol compound and carbonic acid diester is supplied in a vertical-type churning reactor. (1) — reserve polycondensation process: — After performing the polycondensation reaction of mixture and manufacturing the 1st prepolymer of viscosity average molecular weight 3,000-10,000, (2) — last polycondensation process: — the 1st prepolymer obtained at the process of the above (1) It leads to the vertical-type churning reactor possessing a double helical ribbon aerofoil, and a polycondensation reaction is performed within this reactor. Viscosity average molecular weight Nothing [ of 10,000-20,000 / the 2nd prepolymer and nothing ], (3) — back polycondensation process: — the 2nd prepolymer of said process (2) — the end lower part of the container longitudinal direction of a horizontal type — It has the inlet port of a processed liquid, an outlet, and the exhaust port of volatile matter in the other end lower part and the upper part, respectively. Install two rotation \*\*\*\* in the longitudinal direction both ends inside a container side by side, connect two or more cylindrical rectangle frames with each of this rotation \*\*\*\*, and a skeleton pattern impeller is formed. It leads in the horizontal-type reactor which approaches inside the impeller of the other party and rotates so that this impeller may gear mutually. A polycondensation reaction is performed and the manufacture approach of the aromatic series polycarbonate resin which is the amount of nearby giant molecules and is characterized by viscosity average molecular weight obtaining the aromatic series polycarbonate resin of 15,000-40,000 from the 2nd prepolymer of the above (2) is offered.

[0010]

[Function] Churning of a prepolymer and a polymer is fully performed, a rate of reaction is quick and an aromatic series polycarbonate with little coloring can be manufactured more in the amount of giant molecules.

[0011]

[Embodiment of the Invention] Hereafter, the manufacture approach of the aromatic series polycarbonate concerning this invention is explained concretely. In this invention, an aromatic series diol compound and carbonic acid diester are used as a raw material which manufactures an aromatic series polycarbonate.

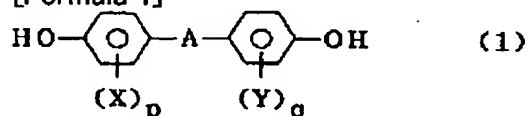
Aromatic-series diol compound: The aromatic series diol compound used in manufacture of this invention is a compound shown by the general formula (1).

[0012]

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[Formula 1]



[0013] the inside of a formula, and A — the shape of a straight chain which is not permuted [ the permutation of single bond and carbon numbers 1-10, or ], the letter of branching, or an annular divalent hydrocarbon group — And it is what is chosen from the group which consists of a divalent radical shown by -O-, -S-, -CO-, -SO-, and -SO<sub>2</sub>-. it differs mutually, and is chosen out of hydrogen, a halogen, or the hydrocarbon group of carbon numbers 1-6, and p and q of X and Y are [ the same or ] the integers of 0-2.

[0014] If some examples of representation are given, for example Screw (4-hydroxy diphenyl) methane, 2 and 2-screw (4-hydroxyphenyl) propane, 2, and 2-screw (4-hydroxy-3-methylphenyl) propane, 2 and 2-screw (4-hydroxy-3-t-butylphenyl) propane, 2 and 2-screw (4-hydroxy - 3, 5-dimethylphenyl) propane, 2 and 2-screw (4-hydroxy - 3, 5-dibromo) propane, 4, and 4-screw (4-hydroxyphenyl) heptane, Biphenol, such as a bisphenol; 4, such as 1 and 1-screw (4-hydroxyphenyl) cyclohexane, 4'-dihydroxy biphenyl -3, 3', 5, 5'-tetramethyl-4, and 4'-biphenyl; A screw (4-hydroxyphenyl) sulfone, They are a screw (4-hydroxyphenyl) sulfide, the screw (4-hydroxyphenyl) ether, a screw (4-hydroxyphenyl) ketone, etc. 2 and 2-screw (4-hydroxyphenyl) propane is desirable also in these.

[0015] When it can also perform using together two or more sorts of these compounds (copolymer) and is going to manufacture the letter aromatic series polycarbonate of branching, copolymerization of the polyhydric phenol more than trivalent [ little ] can be carried out. Moreover, monohydric phenol, such as p-t-butylphenol and p-cumyl phenol, can also be used for the closure of a hydroxyl-group end for the purpose of raising further the thermal stability and hydrolysis-proof nature of the aromatic series polycarbonate manufactured.

[0016] Carbonic acid diester; as carbonic acid diester, there are dimethyl carbonate, diphenyl carbonate, JITORIRU carbonate, screw (4-KURORU phenyl) carbonate, screw (2, 4, 6-TORIKURORU phenyl) carbonate, etc. As for these carbonic acid diester compound, it is common to be superfluously used to one mol of aromatic series diol compounds, and it is desirable to use in the amount of 1.02-1.20 mols preferably 1.01-1.30 mols.

[0017] Ester interchange catalyst; in the melt polycondensation reaction of an aromatic series diol compound and carbonic acid diester, an ester interchange catalyst is usually used. Specifically as such an alkali metal compound and an alkaline-earth-metal compound with desirable as this ester interchange catalyst an alkali metal compound, an alkaline-earth-metal compound, quarternary ammonium salt, and phosphonium salt being used, the organic salt acid of alkali metal and alkaline earth metal, a mineral salt acid, an acid compound, a hydroxide, a hydride, or an alcoholate is mentioned preferably.

[0018] More specifically as an alkali metal compound A sodium hydroxide, a potassium hydroxide, a lithium hydroxide, a sodium hydrogencarbonate, A potassium hydrogencarbonate, a carbonic acid hydrogen lithium, a sodium carbonate, potassium carbonate, A lithium carbonate, the disodium salt of bisphenol A, 2 potassium salt, 2 lithium salt, the sodium salt of a phenol, potassium salt, lithium salt, Inorganic cesium salts, such as cesium hydroxide, cesium carbonate, and carbonic acid hydrogen caesium, Phenols cesium salts, such as alcoholic cesium salts, such as organic-acid cesium salts, such as acetic-acid caesium and stearin acid caesium, caesium MECHIRETO, and caesium ethylate, caesium phenolate, and a JISESHIUMU salt of bisphenol A, etc. are mentioned.

[0019] Moreover, as an alkaline earth metal compound, a calcium hydroxide, a barium hydroxide, a magnesium hydroxide, a strontium hydroxide, calcium hydrogencarbonate, barium hydrogen carbonate, carbonic acid hydrogen magnesium, carbonic acid hydrogen strontium, a calcium carbonate, a barium carbonate, a magnesium carbonate, a strontium carbonate, etc. are mentioned concretely. These compounds are independent, or are combined and used.

[0020] In this invention, a basic compound can also be used with the above alkali metal

compounds and/or alkaline-earth-metal compounds as a catalyst. As such a basic compound, it is easily decomposability or volatility, for example at an elevated temperature, and it is rare to remain to the last aromatic series polycarbonate, and the nitrogen-containing basicity compound and phosphonium hydroxide compound which do not have a bad influence on physical properties, such as a hue, are mentioned, and, specifically, the following compounds are mentioned.

[0021] As a nitrogen-containing basicity compound, tetramethylammonium hydroxide ( $\text{Me}_4\text{NOH}$ ), Alkyls, such as tetraethylammonium hydroxide ( $\text{Et}_4\text{NOH}$ ), The ammonium hydroxide which has aryl, the Al aryl group, etc. the third class amines, such as a trimethylamine and triethylamine, and  $\text{R}_2\text{NH}$  (the inside R of a formula — methyl —) aryl groups, such as alkyls, such as ethyl, phenyl, and toluyl one, etc. — it is — the second class amines shown — Primary amine, 2-methylimidazole which are shown by  $\text{RNH}_2$  (it is the same as the above the inside R of a formula), An iminocarboxylic acid derivative or its salts, such as imidazole derivatives, such as 2-phenylimidazole, and nitrilotriacetic acid sodium, Or basic salt, such as ammonia, tetramethylammonium borohydride ( $\text{Me}_4\text{NBH}_4$ ), and tetrabutylammonium borohydride ( $\text{Bu}_4\text{NBH}_4$ ), is raised.

[0022] Moreover, as a phosphonium hydroxide compound, tetraethyl phosphonium hydroxide, tetrabutyl phosphonium hydroxide, tetraphenylphosphonium hydroxide, methyltriphenylphosphonium hydroxide, allyl compound triphenylphosphonium hydroxide, etc. are raised.

[0023] Tetra-alkylammonium hydroxide, tetrabutyl phosphonium hydroxide, and tetraphenylphosphonium hydroxide are used preferably among these. When a basic compound is used as a catalyst,  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  — one mol of basic compounds is usually preferably used to one mol of aromatic series diol compounds in the amount of  $1 \times 10^{-5}$  to  $1 \times 10^1$  — two mols.

[0024] The production process of an aromatic-series polycarbonate: In this invention, the polycondensation reaction of an aromatic series diol compound and carbonic acid diester is performed through at least two steps of processes using a vertical-type churning reactor and a horizontal-type reactor, as shown in drawing 1.

Reserve polycondensation process : (1) Supply the melting mixture of an aromatic series diol compound and carbonic acid diester in a vertical-type churning reactor. After performing the polycondensation reaction of mixture and manufacturing the 1st prepolymer of viscosity average molecular weight 3,000–10,000, The 1st prepolymer obtained at said process is led to the vertical-type churning reactor possessing a double helical ribbon aerofoil. (2) — last polycondensation process: — A polycondensation reaction is performed within this reactor. Viscosity average molecular weight Nothing [ of 10,000–20,000 / the 2nd prepolymer and nothing ], (3) — back polycondensation process: — the 2nd prepolymer obtained at said process (2) — the end lower part of the container longitudinal direction of a horizontal type — It has the inlet port of a processed liquid, an outlet, and the outlet of volatile matter in the other end lower part and the upper part, respectively. Install two rotation \*\*\*\* in the longitudinal direction both ends inside a container side by side, connect two or more cylindrical rectangle frames with each of this rotation \*\*\*\*, and a skeleton pattern impeller is formed. It leads in the horizontal-type reactor which approaches inside the impeller of the other party and rotates so that this impeller may gear mutually, a polycondensation reaction is performed, from the 2nd prepolymer of (2), it is the amount of nearby giant molecules, and viscosity average molecular weight obtains the aromatic series polycarbonate resin of 15,000–40,000. In the above, in the reserve polycondensation process of (1), if the vertical-type churning reactor possessing the double helical ribbon aerofoil used at the last polycondensation process of (2) as a vertical-type churning reactor is used, it can carry out at at least two steps of processes.

[0025] Drawing 1 shows the flow sheet of this invention. the inside of drawing, and 1 — raw material installation tubing and 2 — in a vertical-type reactor and 5, an impeller and 6 show a double helical ribbon aerofoil, 7 shows [ ester conversion catalyst installation tubing and 3 / by-product exhaust pipe, 4, and 4' ] the partial horizontal sectional view of a horizontal-type reactor, and, for the 1st prepolymer and 10, as for a final product polymer and 12, the 2nd prepolymer and 11 are [ 8 / a grid aerofoil and 9 / a driver and 13 ] shaft seals. the horizontal-type reactor 7 — the lower part of both ends — respectively — the entry (20) of the 2nd

prepolymer, and an outlet (21) — there is an exhaust port 3 of volatile matter in the upper part further (neither is illustrated in Fig. 1). Drawing 2 is the expanded sectional view of vertical-type reactor 4' possessing the double helical ribbon aerofoil 6. The screw section to which raw material (prepolymer) installation tubing and 15 send out a revolving shaft, and, as for 14, 16 sends out a prepolymer, and 17 are the deliveries of a prepolymer among drawing. Drawing 3 is the A-A sectional view of the horizontal-type reactor 7 in drawing 1. Drawing 4 is the perspective view of the grid aerofoils 8 and 8 in this horizontal-type reactor.

[0026] (1) Reserve polycondensation process : although reactor 4' which possesses a double helical ribbon aerofoil after the viscosity average molecular weight of the prepolymer to generate became 3,000 or more is used in this invention, the equipment of arbitration can be used until it reaches this viscosity average molecular weight. For example, the mixing vessel type thing possessing the Max blend aerofoil (chemical engineering \*\*\*\*, 911 pages of the 5th edition of revision; \*\*\*\*\*) of a configuration in alignment with the inside of the low wall of a turbine blade, a paddle aerofoil, a support aerofoil, a helical ribbon aerofoil, a double helical ribbon aerofoil, and a tub and a side attachment wall etc. can be used. Moreover, the number of reaction vessels is 2 - 5 tub extent. The reaction in the reserve polycondensation reactor of the 1st step The raw material installation tubing 1 is minded for melting mixture with the diphenyl carbonate as 2 and 2-screw (4-hydroxyphenyl) propane and carbonic acid diester as an aromatic series diol compound the bottom of inert gas, for example, nitrogen-gas-atmosphere mind. Moreover, the alkali metal compound, the alkaline-earth-metal compound, and/or the basic compound of a catalyst are supplied through the catalyst installation tubing 2 in the vertical-type churning reactor 4 possessing the above-mentioned impeller 5, and a reaction is advanced, removing a by-product from the by-product exhaust pipe 3. Reactors 4 and 4 can be divided even into two tubs - 5 tub extent, and a polymerization can also be continuously advanced until viscosity average molecular weight amounts to 3,000-10,000. Moreover, the range of 100-300 degrees C of reaction temperature in the meantime is 180-280 degrees C preferably, and reaction pressure is the range to ordinary pressure - 1Torr.

[0027] (2) the viscosity average molecular weight 3,000-10,000 obtained by last polycondensation process; next the above-mentioned actuation — preferably, supply the aromatic series polycarbonate resin (the 1st prepolymer) of 5,000-8,000 to vertical-type reactor 4' possessing the double helical ribbon aerofoil 6, and advance a reaction further, making the phenol which carries out a byproduction distill off out of a system. A wing diameter, comparable, and a ribbon span (b/d) have [ the dimension specification of a double helical ribbon aerofoil / about 0.85 to 0.95 path clearance (d/D), and an aerofoil pitch (L/d) ] about 0.08 to 0.12 thing almost as desirable as 0.95-1.05. The gaseous-phase section 18 exists in this vertical-type reactor 4' upper part, and the phenol which carries out a byproduction has structure in which discharge 3 is possible. Moreover, it is in the equipment side-attachment-wall liquid phase section, the draw opening 17 has a desirable thing in the bottom of the tank section, and the feed opening 14 of the 1st prepolymer has that still more desirable by which the screw type polymer discharge machine 16 is introduced into draw opening of this bottom of the tank section. The range of 200-320 degrees C of reaction temperature is 240-300 degrees C preferably, and 10 or less Torrs of reaction pressure are preferably controlled to 1 or less Torr. Moreover, an aerofoil rotational frequency can shorten polymerization time amount by setting a rotational frequency as extent which processing liquid does not \*\*\*\*\* with 10 - 100rpm extent at a high speed. Reaction time is the range for 30 - 120 minutes, and viscosity average molecular weight usually increases it by 7,000 or more preferably or more by 5,000 by this polymerization. the 2nd prepolymer obtained — viscosity average molecular weight 10,000-20,000 — it is 13,000-18,000 preferably.

[0028] (3) Back polycondensation process; then the 2nd prepolymer obtained by the above-mentioned reaction actuation It has the inlet port 20 of a processed liquid, an outlet 21, and the exhaust port 3 of volatile matter substantially, respectively in the end lower part, the other end lower part, and the upper part of a longitudinal direction of a horizontal type. [ of a container 19 ] Install two revolving shafts 8a and 8b in the longitudinal direction both ends inside a container side by side, connect two or more cylindrical rectangle frames 8 and 8 with each of this revolving

shaft, and a skeleton pattern impeller is formed. A reaction is advanced further, making the phenol which supplies and carries out a byproduction to the horizontal-type reactor which approaches inside the impeller of the other party and rotates distill off so that this impeller may gear mutually. A polymer is discharged with the exhaust of the liquid phase section of a horizontal-type reactor end, and the screw type which was preferably supplied from the end lower part 20, and was formed in the other end lower part. The gaseous-phase section 22 for making the phenol which carries out a byproduction distill out of the processing liquid of the shape of a thin film formed of churning, and discharge Rhine 3 are established in the equipment upper part. Moreover, in order that the configuration of the equipment lower part may lose the dead space of processing liquid, the so-called reverse heart mold configuration where the radius of curvature of the rotating cylindrical rectangle frames 8 and 8 was met is desirable (refer to drawing 3).

[0029] Vertical 8' / 8" wide of the cylindrical rectangle frame 8, the rectangle frame with which a proportion adjoins about by one to three is a 90-degree phase angle, and it is desirable to connect so that an impeller may become short in the connection direction (flow direction of a polymer). A connection number of stages is made into about 4-12 steps. Moreover, these two impellers rotate at the same rate in the different direction so that it may approach mutually and may run through its other party upwards from the bottom. A rotational frequency is 3 - 30rpm extent. The range of 200-320 degrees C of reaction temperature is 240-300 degrees C preferably, and 10 or less Torrs of reaction pressure are preferably controlled to 1 or less Torr. By this polymerization, viscosity average molecular weight usually increases reaction time by 5,000 or more preferably or more by 3,000 in the range for 30 - 120 minutes.

[0030] the aromatic series polycarbonate resin discharged from the horizontal-type reactor 7 — viscosity average molecular weight — 15,000-40,000, and a polymer with Hue YI are 20,000-35,000 preferably and good [ the hue in the 1.8 or less amount of macromolecules ] — it is — after degassing cooling — \*\*\*\*\* — it is-izing and collected. 10-20 ppm and a phenol are carrying out [ diphenyl carbonate / 40-100 ppm, 2, and 2-screw (4-hydroxyphenyl) propane ] the 5 ppm or less extent residual of the aromatic series polycarbonate resin 11 collected at this time.

[0031] Additives, such as the usual heat-resistant stabilizer, an ultraviolet ray absorbent, a release agent, an antistatic agent, a slipping agent, an anti blocking agent, lubricant, an antifogger, natural oil, synthetic oil, a wax, an organic system bulking agent, and an inorganic system bulking agent, may be added to the aromatic series polycarbonate resin obtained by this invention. Such an additive remelts the aromatic series polycarbonate resin which could also add to the aromatic series polycarbonate resin in a melting condition, and it once pelletized, and can also be added. In addition, as for remelting, it is desirable to carry out under an inert gas ambient atmosphere.

[0032] Operation of each process of this invention may have continuous system, a batch process, the combination type of continuation and a batch, etc., and which approach may be used for it.

[0033]

[Example] Hereafter, although an example explains this invention, this invention is not limited to these examples. Analysis of the aromatic series polycarbonate resin obtained by this invention was performed with the following measuring method.

(1) Using the viscosity-average-molecular-weight ubellohde's viscosimeter, 20-degree C limiting viscosity [eta] was measured among the methylene chloride, and it asked from the following formulas.

[eta] =  $1.23 \times 10^{-4} \times (\text{Mv})^{0.83}$  (2) 10% methylene chloride solution of hues was put into the glass cel with a diameter [ of 25mm ], and a height of 55mm, the tristimulus values XYZ which are absolute values of a color were measured with the color circuit tester (SC[ by Suga Test Instruments Co., Ltd. ]-1- CH), and YI value which is the index of whenever [ yellow ] was calculated with the following relational expression.

$YI = 100 / Y(1.28X - 1.06Z)$

Coloring, so that this YI value is large is shown.



[0034] The melting mixture which carried out mixed preparation of bisphenol A and the diphenyl carbonate under example 1 nitrogen-gas-atmosphere mind at the rate of a constant ratio (diphenyl carbonate / bisphenol A (mole ratio) = 1.050) by the flow rate of 403.03 mols/o'clock in all The Max blend aerofoil shown in drawing 1 through raw material installation tubing is provided. Ordinary pressure, Continuation supply was carried out under nitrogen-gas-atmosphere mind into the 1st vertical-type churning reaction vessel with a capacity of 100l. controlled at 210 degrees C, and oil-level level was kept constant, controlling the bulb opening prepared in polymer discharge Rhine of the bottom of the tank section so that mean flow-time becomes in 30 minutes. Moreover, while starting supply of the above-mentioned raw material mixture, continuation supply of 2% of the cesium carbonate water solution was carried out as a catalyst by the flow rate of 3.2ml (it is 1xten - six mols to one mol of bisphenol A)/o'clock. The 2nd prepolymer which continuation supply of the polymerization liquid (prepolymer) discharged from the bottom of the tank was carried out serially at the vertical-type churning reaction vessel with a capacity of 100l. which possesses the Max blend aerofoil of the 2nd, the 3rd, and 4 and 4 succeedingly, and 4th with a capacity [ possessing a double helical ribbon aerofoil ] of 100l. vertical-type churning reaction-vessel 4', and was extracted from the 4th reaction-vessel 4' pars basilaris ossis occipitalis was formed into after [ cooling ] pelletizing. between reactions — the [ the 2nd - ] — distilling off of a phenol which controls oil-level level by adjustment of the bulb opening prepared in prepolymer discharge Rhine of the bottom of the tank section so that the mean flow-time of 4 each reaction vessel becomes 60 minutes, and carries out a byproduction to coincidence was also performed. the [ the 2nd - ] — the reaction conditions in 4 each reaction vessel are the 2nd reaction vessel (210 degrees C, 100Torr, 110rpm), the 3rd reaction vessel (240 degrees C, 15Torr, 75rpm), and the 4th reaction vessel (280 degrees C, 0.5Torr, 25rpm), respectively, and carried out conditioning to the elevated temperature, the high vacuum, and the low agitating speed with advance of a reaction. The dimension specifications of a double helical ribbon aerofoil were path clearance (d/D) 0.90, the aerofoil pitch (L/d) 1.00, and the ribbon span (b/D) 0.10. The viscosity average molecular weight of the prepolymer extracted from the 3rd and 4 reaction vessel was 6,200 and 16,100, respectively, and mean-flow-time time amount was 3.5 hours a total. Next, carrying out melting with the single screw extruder which controlled the 2nd prepolymer pellet obtained by the above-mentioned actuation at 280 degrees C Continuation supply is carried out at the rate of 6 kg/Hr at the horizontal-type reactor 7 (Hitachi, Ltd. make "a grid aerofoil polymerization machine" (trade name)) shown in drawing 1 with a capacity of 27l. controlled to 290 degrees C, 0.5Torr, and aerofoil rotational frequency 10rpm, drawing 3, and drawing 4. By [ which prepared in the polymer discharge section of a horizontal-type reactor so that mean flow-time might become in 60 minutes ] extracting and adjusting the engine speed of a screw, the polymer oil-level level 23 in a horizontal-type reactor was kept constant. Continuous running was carried out for about 4 hours until aging of the quality of the polymer 11 discharged after starting prepolymer supply was lost. The viscosity average molecular weight of the obtained aromatic series polycarbonate resin was 30,100, and Hue YI was 1.5.

[0035] Except having changed the double helical ribbon aerofoil 6 of 4th vertical-type churning reaction-vessel 4' for the Max blend aerofoil in example of comparison 1 example 1, it carried out by the same reaction condition as an example, and aromatic series polycarbonate resin was obtained. The viscosity average molecular weight of the polymer in the inlet port of the 4th vertical-type mixing vessel and an outlet was 6,200 and 12,200, respectively, and the viscosity average molecular weight of the aromatic series polycarbonate resin obtained from the horizontal-type reactor was 27,300, and Hue YI was 1.6.

[0036] In order to raise to the same viscosity average molecular weight as an example in the example 1 of example of comparison 2 comparison, except having made mean flow-time in 4th vertical-type churning reaction-vessel 4' equipped with the Max blend aerofoil into 1.5 hours, it carried out by the same reaction condition as the example 1 of a comparison, and aromatic series polycarbonate resin was obtained. Although the viscosity average molecular weight of the polymer in the inlet port of the 4th vertical-type mixing vessel and an outlet was 6,200 and 15,700, respectively and the viscosity average molecular weight of the aromatic series

polycarbonate resin obtained from the horizontal-type reactor was 29,800, compared with the example 1, the fall of a hue was able to see Hue YI in 2.3.

[0037] In example of comparison 3 example 1, the horizontal-type reactor 7 was transposed to the self-cleaning type 2 shaft reactor (Mitsubishi Heavy Industries, Ltd. make "SCR" (trade name)) with a capacity of 2l., and aromatic series polycarbonate resin was obtained by the same reaction condition as an example except having made the speed of supply of an aromatic series polycarbonate prepolymer pellet into 1 kg/Hr, as it had been 60 minutes about mean flow-time. The viscosity average molecular weight of the aromatic series polycarbonate resin obtained from this horizontal-type reactor was 31,900, and Hue YI was 3.8.

[0038] The place which continuation supply was carried out [ place ] at the 5th vertical-type churning reaction vessel which replaced with the grid aerofoil polymerization machine the prepolymer extracted from 4th vertical-type churning reaction-vessel 4' in example of comparison 4 example 1, and possesses the double helical ribbon aerofoil under the same specification as the 4th vertical-type reaction vessel, and reaction-of-identity conditions succeedingly, and made the reaction continue. About 60 minutes after starting polymer supply to the 5th reaction vessel, the churning motor carried out a trip halt, and continuation of a reaction became impossible.

[0039] Except having changed the double helical ribbon aerofoil of 4th vertical-type churning reaction-vessel 4' for the single helical ribbon aerofoil in example of comparison 5 example 1, it carried out by the same reaction condition as an example 1, and aromatic series polycarbonate resin was obtained. The viscosity average molecular weight of the polymer in the inlet port of the 4th vertical-type mixing vessel and an outlet was 6,200 and 9,600, respectively, and the viscosity average molecular weight of the aromatic series polycarbonate resin obtained from the horizontal-type reactor was 21,800, and Hue YI was 1.4. When a single helical ribbon aerofoil is used, it is difficult to obtain the aromatic series polycarbonate of the amount of giant molecules.

[0040]

[Effect of the Invention] According to the manufacture approach of the aromatic series polycarbonate resin by this invention, it excels in a hue and the aromatic series polycarbonate resin of the amount of giant molecules can be obtained.

**[Brief Description of the Drawings]**

**[Drawing 1]** It is the flow sheet Fig. of the manufacture approach of this invention.

**[Drawing 2]** It is the sectional view showing the vertical-type churning reactor possessing a double helical ribbon aerofoil.

**[Drawing 3]** It is the A-A sectional view of the drawing 1 horizontal-type reactor.

**[Drawing 4]** It is the perspective view of the skeleton pattern impeller of a horizontal-type reactor.

**[Description of Notations]**

1 Raw Material Installation Tubing

4 Vertical-Type Reactor

5 Impeller

6 Double Helical Ribbon Aerofoil

7 Horizontal-Type Reactor

8 Skeleton Pattern Impeller

9 1st Prepolymer

10 2nd Prepolymer

11 Polycarbonate Resin

14 1st Prepolymer Charging Hole

17 2nd Prepolymer Exhaust Port

18 Gaseous-Phase Section



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